UM 320639-1-P

Annual Report

COMBUSTION OF UNCONFINED NATURAL GAS - AIR CLOUDS

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Research Project No. 5010-362-0034

May 1979

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RESEARCH PROJECT NO. 5010-362-0034

Annual Report, April 1979

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FOREWORD

This report covers the progress made on GRI Contract No. 5010-362-0034 during the year 1978. Some of the results appear in more detailed form in various publications and these are referenced where pertinent. However, a somewhat less detailed coverage of the results is presented herein.

The research investigation is currently funded to the end of 1979 under GRI Contract No. 5014-363-0132.

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ABSTRACT

The progress that was made in 1978 on the study of the blast wave initiation of detonation in natural gas - air clouds is presented. Experimental results relating to the initiation energy requirements for the detonation of methane - oxygen - nitrogen mixtures are described and discussed. Similar results are presented for the case of methane - ethane - air mixtures. The status of the theoretical study relating to the prediction of the critical initiation energy is described. These studies include a fairly comprehensive analysis as well as an ultra - simplified version. Publications, presentations, and pertinent related activities during the year are listed.

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INTRODUCTION

The transportation and storage of large amounts of liquified natural gas (LNG) presents the possibility of tank rupture and, hence, spillage or leakage. The resulting cloud that is formed may conceivably be ignited by hot chimney gases, an open flame, electrical equipment, etc. In these cases it is most likely that a deflagration wave will be initiated which, in itself, can cause extensive damage as it propagates throughout the cloud. However, the question arises as to whether the deflagration can accelerate and develop into a fully established detonation with the attendant high pressures and velocities. Now in the case of combustion of a mixture under confinement — as, for example, when ignition occurs near the closed end of a constant cross sectional area pipe — the dominant processes are as follows. The flame, in moving away from the closed end, generates lower density products which, by conservation of mass, causes the flame to accelerate and the unburned mixture to be set in motion ahead of the flame. That is, the flame acts like a piston. The accelerating wave transmits weak compression waves into the unburned mixture which raises the pressure and temperature and hence, usually, the rate of combustion. Further, the gas motion generates a boundary layer on the walls of the pipe and, along with this, turbulence. As a consequence, the flame shape is wrinkled and the piston effect is reinforced. If these

dynamic interactions continue, the flame can go through transition to detonation. Now in the case of an unconfined cloud, ignited at a point, there will be a tendency for flame acceleration. However, with no enclosing walls, the boundary layers and high degrees of turbulence will not be generated. Thus it seems very unlikely that a flame would go through a transition to detonation in a completely unconfined cloud. Of course, if localized high turbulence levels existed because of other effects, the flame acceleration mechanism would be present. Or, if there were local confinements, such as pipes, walls, etc., flame acceleration could occur.

Another aspect of this problem is that wherein a large amount of energy is released very rapidly in a localized region. In this case, strong blast waves (shock waves followed by an expansion zone) propagate into the unburned mixture. The Mach number, and hence strength of these waves, may be well above detonation Mach numbers. It is then of interest to know whether detonation will propagate throughout the cloud. In the case of natural gas-air mixtures it has not been clear as to whether detonation can be generated under conditions of no confinement.

In order to shed light on the possibility of achieving detonation of natural gas-air mixtures through blast wave initiation, some large scale tests have been run at the Naval Weapons Center. However, such tests involve great

expense, incomplete control over conditions, very high energy levels, limited diagnostics, and the experiments are limited in number. On the other hand, laboratory scale experiments may suffer from the fact that the distance available for observation may not be sufficient and, also, confinement effects may be present. Accordingly, we have deemed it very important to conduct a carefully controlled experimental study along with a matching theoretical analysis. In the following the experimental aspects are presented first and then followed by the analysis. The predictions of the latter are discussed in reference to the experimental results.

EXPERIMENTAL STUDIES

The experimental work was performed in a unique sectored test chamber that was designed, in an earlier investigation, to model cylindrical unconfined cloud detonations. The original chamber and subsequent alterations to it are described in more detail in a recent paper[1]. The extended chamber is 137.6 cm long in the radial direction, it has an included angle of 20°; and corresponds to a cloud height of 5.21 cm. A sketch of the chamber is shown in Fig. 1. The chamber was charged to ambient pressure and temperature with the desired gaseous mixture, which had been mixed in advance and stored in a separate reservoir. A blasting cap and controlled amount of condensed explosive (Detasheet C, explosive energy release of 3950 joules gm^{-1}) was placed at the apex of the chamber and exploded, thereby sending a

cylindrical blast wave through the mixture. The propagation of a wave front, i.e. time-of-wave arrival, was monitored by means of the 17 pressure switches mounted along the chamber's centerline. An additional pressure switch was placed on the bottom of the chamber wall and it was used to trigger the data acquisition system. It also provided the reference time point, i.e. relative time, $t' = 0$ at $r = 12.70$ cm.

In the previous year, attempts to detonate stoichiometric methane-air mixtures in this experimental facility were unsuccessful. The explosive initiator energy was limited to about six grams in the laboratory. Experiments then followed which utilized stoichiometric methane-oxygen mixtures diluted with varying amounts of nitrogen; i.e. $CH_4 + 2O_2 + XN_2$ ($X = 7.52$ for air). For small amounts of nitrogen, detonation was readily achieved and the initiator energy was determined, by a large number of go-no go experiments, for each mixture. As X increased, the critical energy increased exponentially. The results are shown in Fig. 2. Extrapolation of these results to the "air" case indicates that 550 grams of Detasheet (or 7.5×10^6 joules cm^{-1}) would be required to detonate methane-air in our facility; truly an enormous amount.

In recognition of the fact that natural gas usually contains some ethane (although the first constituent to boil-off in the case of a spill would be methane), it was decided to test some stoichiometric methane-ethane-air mixtures. Accordingly the necessary alterations to the

facility were made. The gases were mixed to the desired proportions in a tank, using partial pressure measurements. Later, the mixture was tested by gas chromatography. The mixtures were always stoichiometric but the ratio of ethane to methane was varied. Again, a number of experiments were conducted for each mixture wherein the initiator energy level was varied. In this way the critical energy was determined.

The experimental results obtained for two different energy level runs are shown in Fig. 3. The volummetric ratio of methane to ethane was 2.5. As can be seen, the lower energy level did not initiate detonation, whereas the higher energy level did (i.e. a straight line, or constant velocity wave). The results reported here, and in the following, do not include any correction factor, or efficiency, for the effective energy release.

The range studied was from pure methane-air to pure ethane-air. The results obtained are shown in Fig. 4. The strong sensitivity to small ethane concentrations is readily apparent. Even with small amounts of ethane (1-2% of the mixture, by volume), the mixture is relatively easy to detonate. However, as the ethane concentration becomes smaller than 1%, the initiator energy required increases rapidly. Extrapolation of these results to zero ethane (admittedly subject to appreciable uncertainty) predicts a

value for the detonation of methane-air which is in reasonably good agreement with the earlier results of Nicholls et al.[2] The latter results were obtained in the same apparatus as that used here and the value for methane-air was obtained by extrapolating results for $CH_4 + 2O_2 + xN_2$ mixtures to the air case.

Finally, it is of interest to show the normalized data obtained in this study with that obtained by Bull[3] for the spherical case. Figure 5 shows the threshold energy for a given mixture as compared to that for stoichiometric ethane-air. For the spherical case, E_{oc} has units of energy whereas in the cylindrical case it is energy per unit length. The strong effect of small amounts of ethane is apparent in both cases.

ANALYTICAL STUDIES

The theoretical determination of the "critical initiation energy" or the amount of high explosive needed to initiate a detonation in an unconfined fuel - oxidizer cloud has been the subject of a number of recent investigations as discussed in the review by Lee[4]. The finite difference calculations of Boni et al[5] and Boni and Wilson[6] are, perhaps, the most recent developments. All these theories rest on the basis that initiation depends on the interaction between the decay of the initiating blast and the growth of the induction zone behind the shock front. A key difficulty is determination of a clear - cut criterion for the onset of initiation. Thus Boni et al[5] chose the critical initiation energy by inspecting Mach number - radius trajectories computed for different values of the blast energy using a complex numerical code. The objective of the present analysis has been to simplify the computations and to establish a more precise criterion for the onset of detonations. Two approaches, which are described below, have been used. A relatively detailed model, which requires minimal computational time and provides good agreement with experiment, has been developed. In addition an ultra simplified model which shows the critical initiation energy to be associated with a mathematical singularity in the governing equations has also been explored.

The sudden release of energy due to high explosive or the explosion of a confined portion of natural gas - air cloud results in the formation of an overdriven decaying detonation which propagates into the cloud. In the detailed model this detonation wave is represented by two fronts: a leading shock and then a discontinuous reaction front separated from the shock by the induction distance E_I. An irreversible second order single step reaction is used to represent the induction process between the two fronts.

Two characteristic length scales representing chemical and hydrodynamic flow processes can be identified in this two front model. ℓ_c is a chemical length which is of the order of the induction distance, while the hydrodynamic processes behind the two front detonation may be characterized by the shock radius R_s. For most realistic conditions the ratio ℓ_c/R_s will be small making it possible to formulate simple equations for the induction distance and the flow within the induction zone. The conservation equations can then be used to determine conditions downstream of the two front detonation propagating into the cloud.

On the scale of the radius R_s, the detonation front appears as a discontinuity if $\ell_c/R_s \ll 1$. Hence the flow property between blast center and the front can be calculated using the method developed by Bach et al[7]. A detailed description of the above analysis is presented by Oza[8] in his recent Ph.D. thesis.

Theoretically determined initiation energies based on the above theory were in good agreement with the measured values of Bull et al[9] when the kinetic data of Tsuboi and Wagner[10] was used for the induction zone. This can be seen from Fig. 6 which shows the variation of the critical explosion radius $R_{\Theta_{crit}}$ for methane - oxygen - nitrogen mixtures in the volumetric proportions $CH + 2O_2 + N_2$. If E_{oc} is the critical initiation energy, $R_{o_{crit}}$ is defined as

$$R_{\Theta_{crit}} = \left[E_{oc}/k_\nu \rho_o a_o^2\right]^{1/\nu}$$

where $\nu = 1, 2, 3$ and $k_\nu = 1, 2\pi, 4\pi$ for plane, cylindrical, or spherical geometry, and ρ_o and a_o are the density and speed of sound of the unburned fuel - oxidizer mixture. The choice of R_{oc} in Fig. 6 is based on Lee's suggestion[4] that this parameter should be independent of geometry. It can be seen that theoretical calculations for both spherical and cylindrical geometry are in good agreement with the measurements of Bull et al[9]. The values of $R_{o_{crit}}$ measured in the sectored chamber are higher than these values and probably reflect the effect of the chamber walls. However the trend of $R_{o_{crit}}$ with the amount of nitrogen (i. e. with X) is the same as for the theory and the Bull et al[9] data.

The ultra simplified theory is based on the integral energy conservation equation in the form

$$E + \int_0^{R_s - \ell} \rho Q \, k_\nu r^{\nu-1} dr = \int_\nu^{R_s} \left(\frac{\rho u^2}{2} + \frac{p}{\gamma-1}\right) k_\nu r^{\nu-1} dr$$

where u is the radial velocity, Q the heat of combustion per unit mass of mixture and ℓ is the induction length. As described in detail in the paper by Sichel[11], use of appropriate approximations for these integrals leads to an equation which relates the shock Mach number M_s to the shock radius R_s. This equation has a singularity which depends on the energy E of the initiating explosion. Below a certain critical value E_{cs}, solutions describing transition to a steady detonation become impossible, suggesting that E_{cs} is the critical initiation energy.

It is extremely simple to compute the critical energy E_{cs} with the ultra simple theory, and the theory reproduces the main effects of composition upon the initiation energy E_{cs}. Thus the variation of E_{cs} with equivalence ratio for a methane - air mixture computed with the ultra simple theory is shown in Fig. 7 and has the typical U shape with a minimum near a value of $\Phi = 1$ of the equivalence ratio. Unfortunately, the theory in its present form gives values of E_{cs} which are low. For methane air a value of E_{cs} equivalent to 0.312 kg of tetryl was obtained , while extrapolation of the data of Bull et al[9] suggested a value of 22kg of tetryl.

The ultra simple theory makes it possible to rapidly explore a wide range of initiation phenomena. Because of these attractive features development of this theory is being continued.

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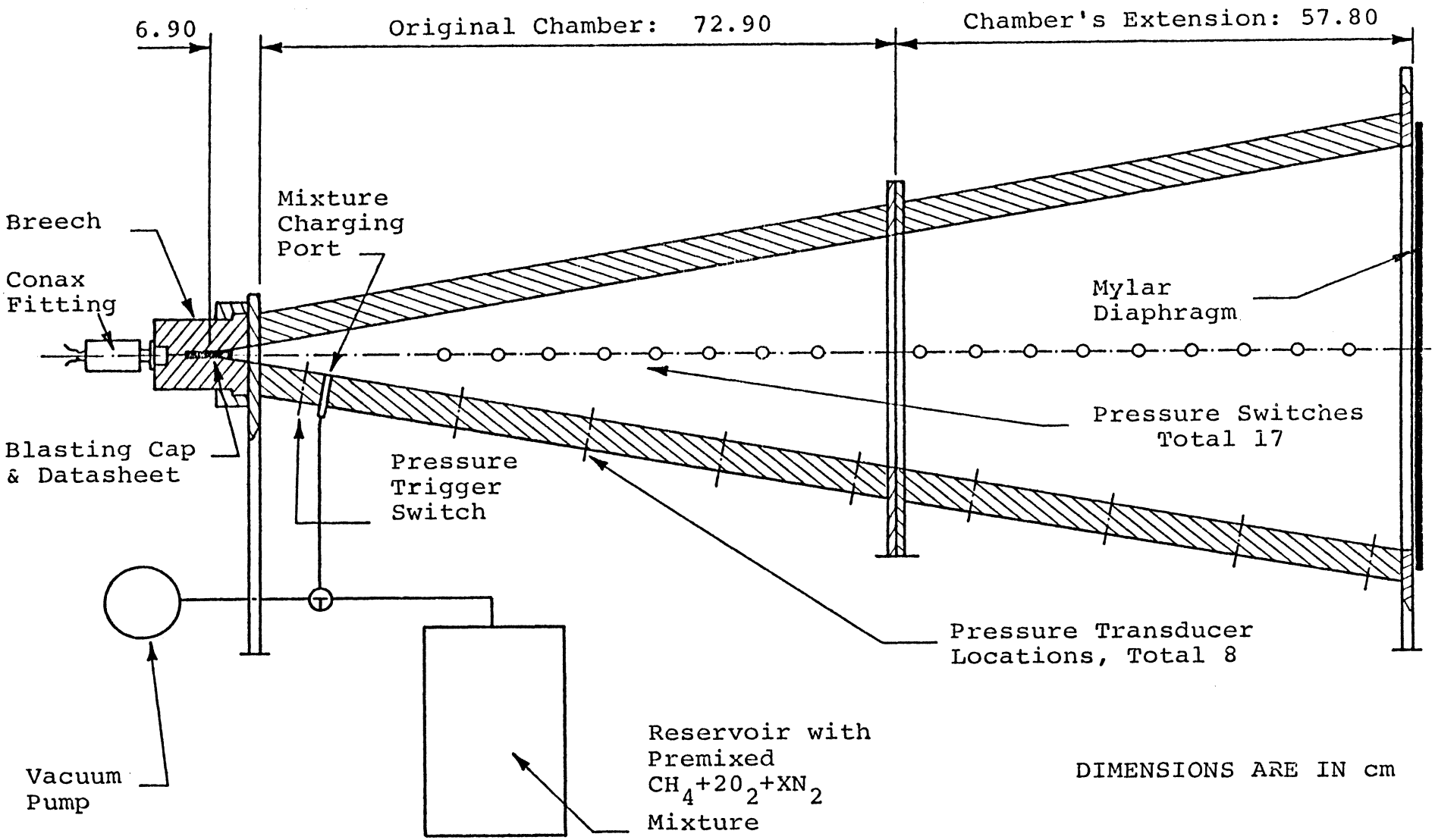

Figure 1. Schematic of Sectored Test Chamber

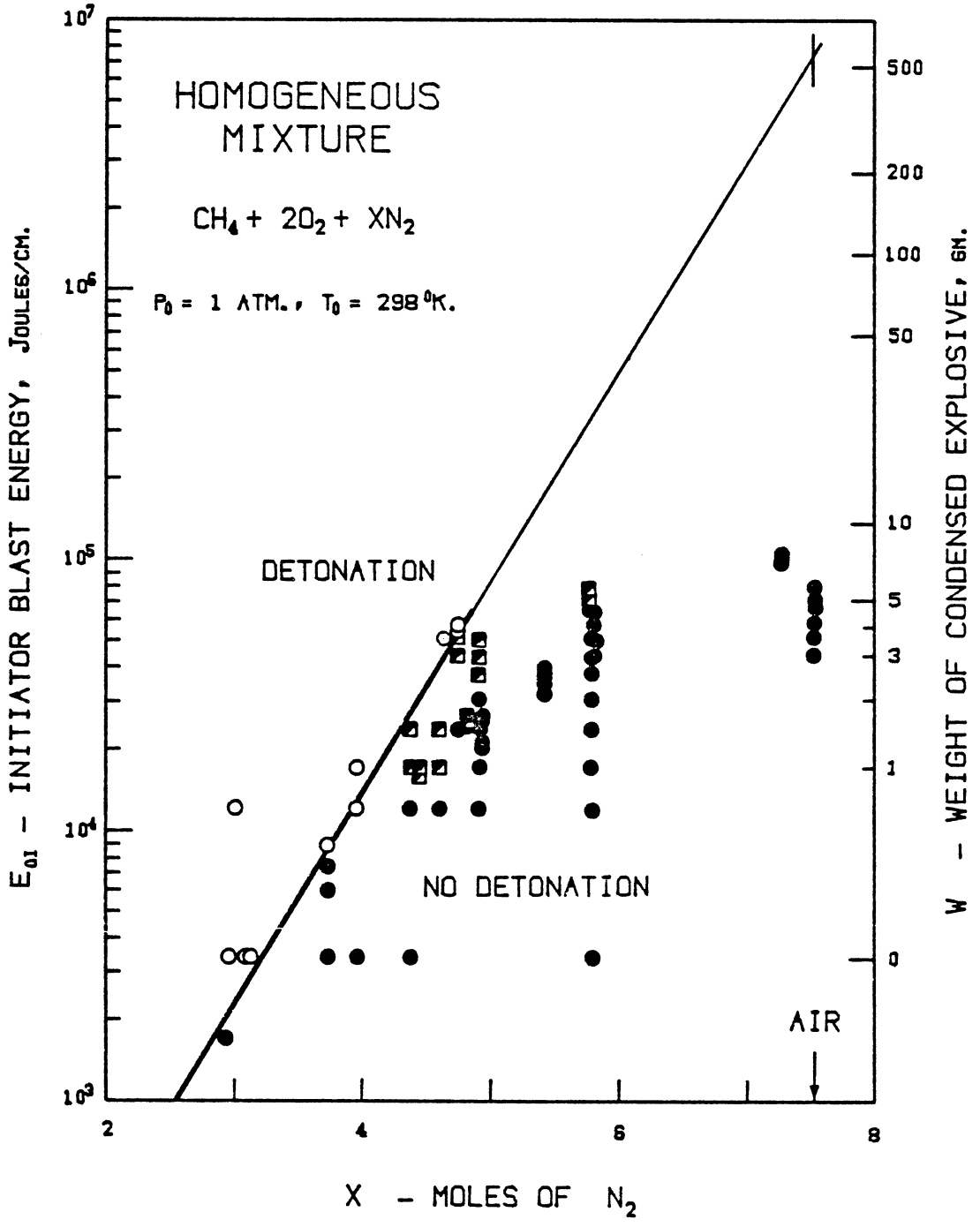

Figure 2. Detonability Limit, Eo_i versus X

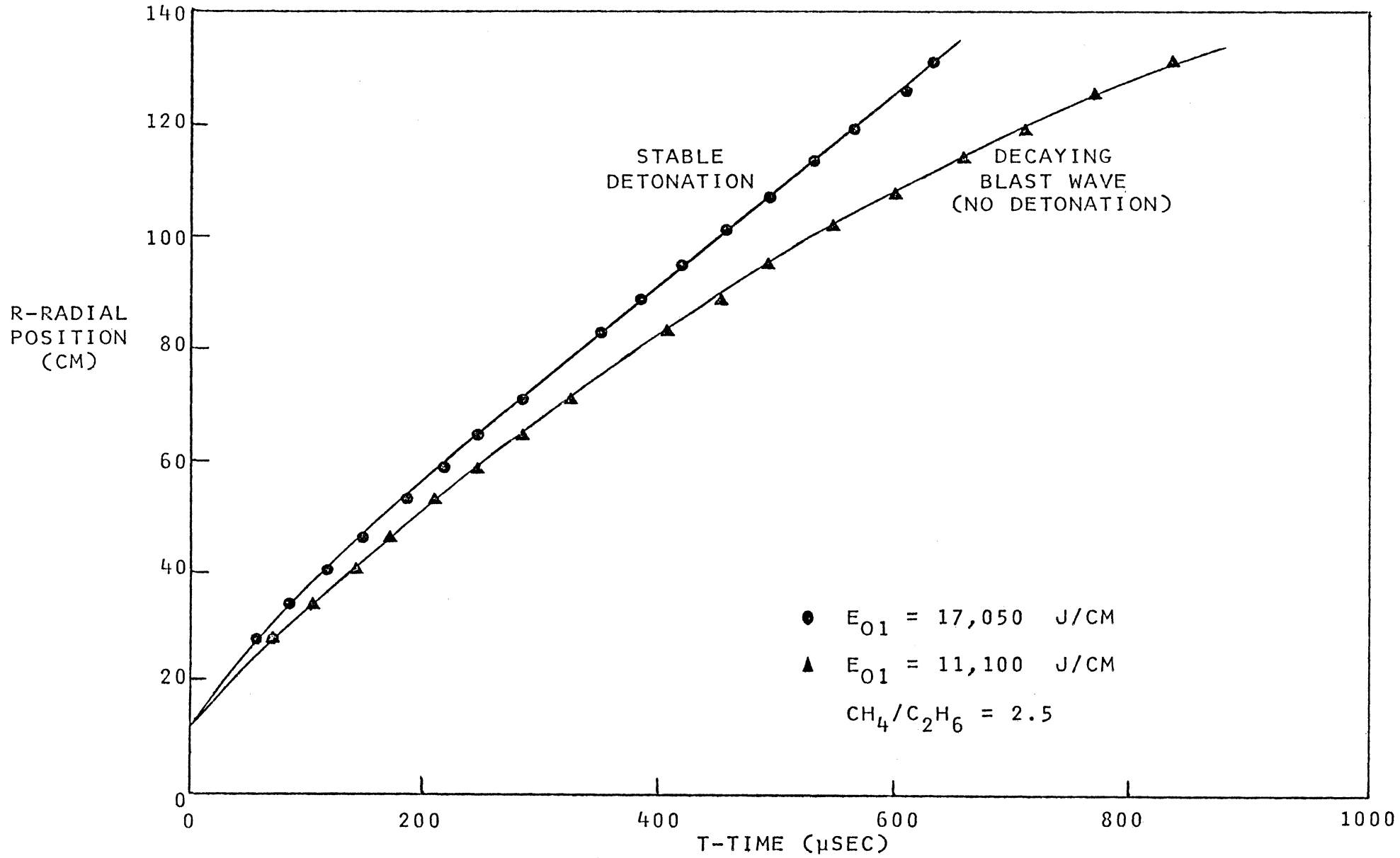

Figure 3. Radius - Time Variation in Methane - Ethane - Air Mixtures

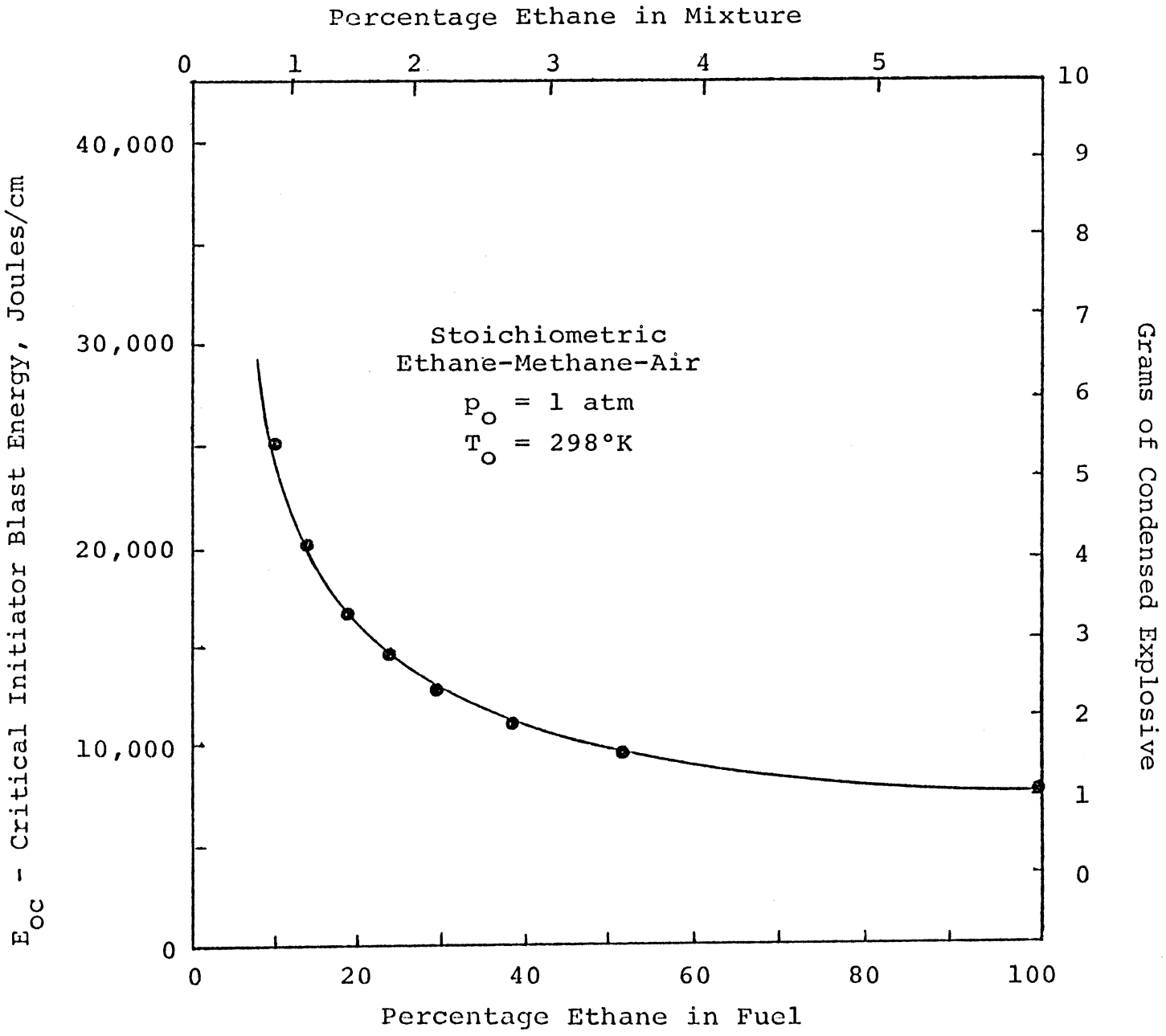

Figure 4. Initiation Energy for Various Stoichiometric Methane-Ethane-Air Mixtures

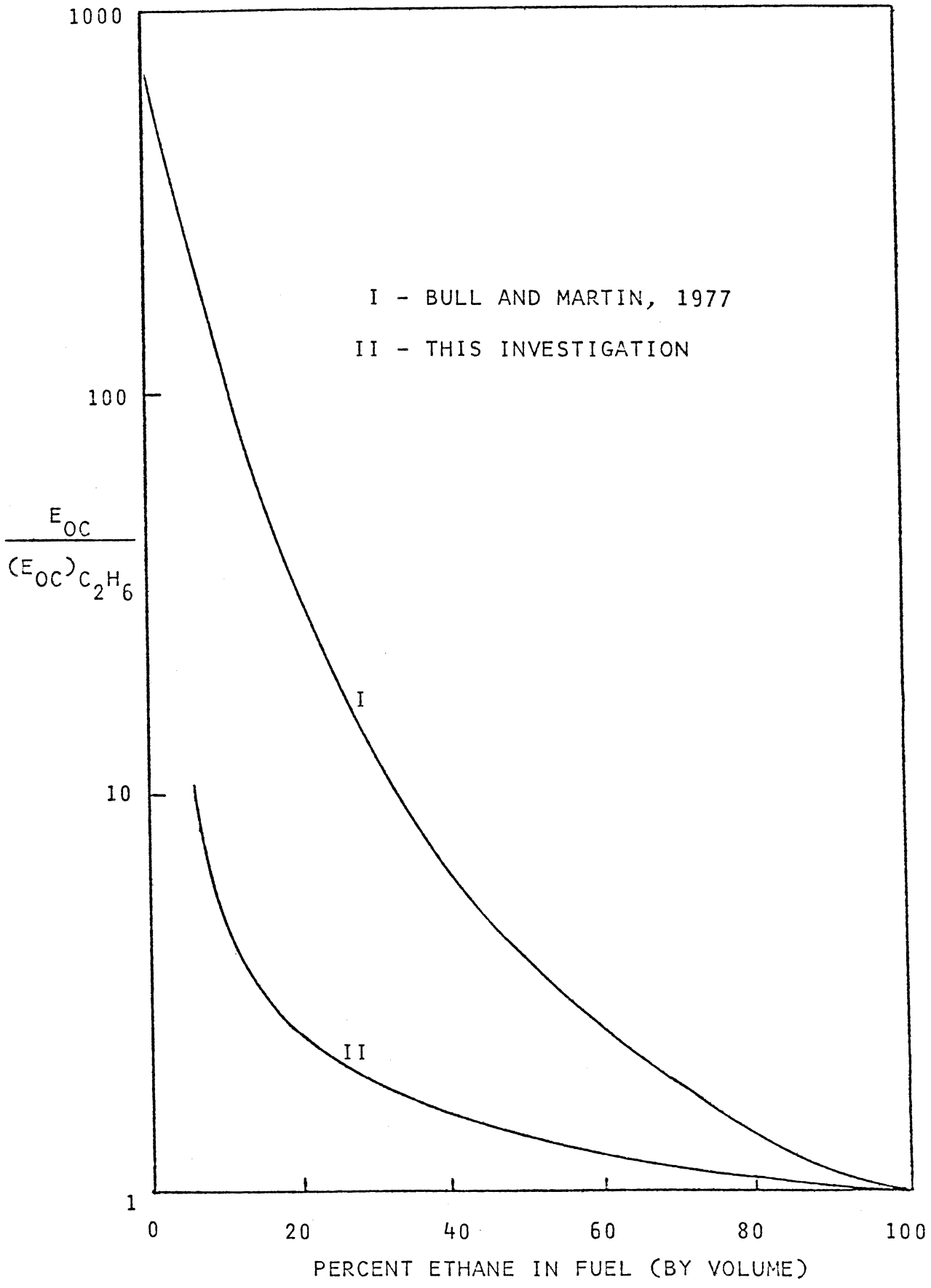

Figure 5. Normalized Critical Energies for Stoichiometric Methane - Ethane - Air Mixtures

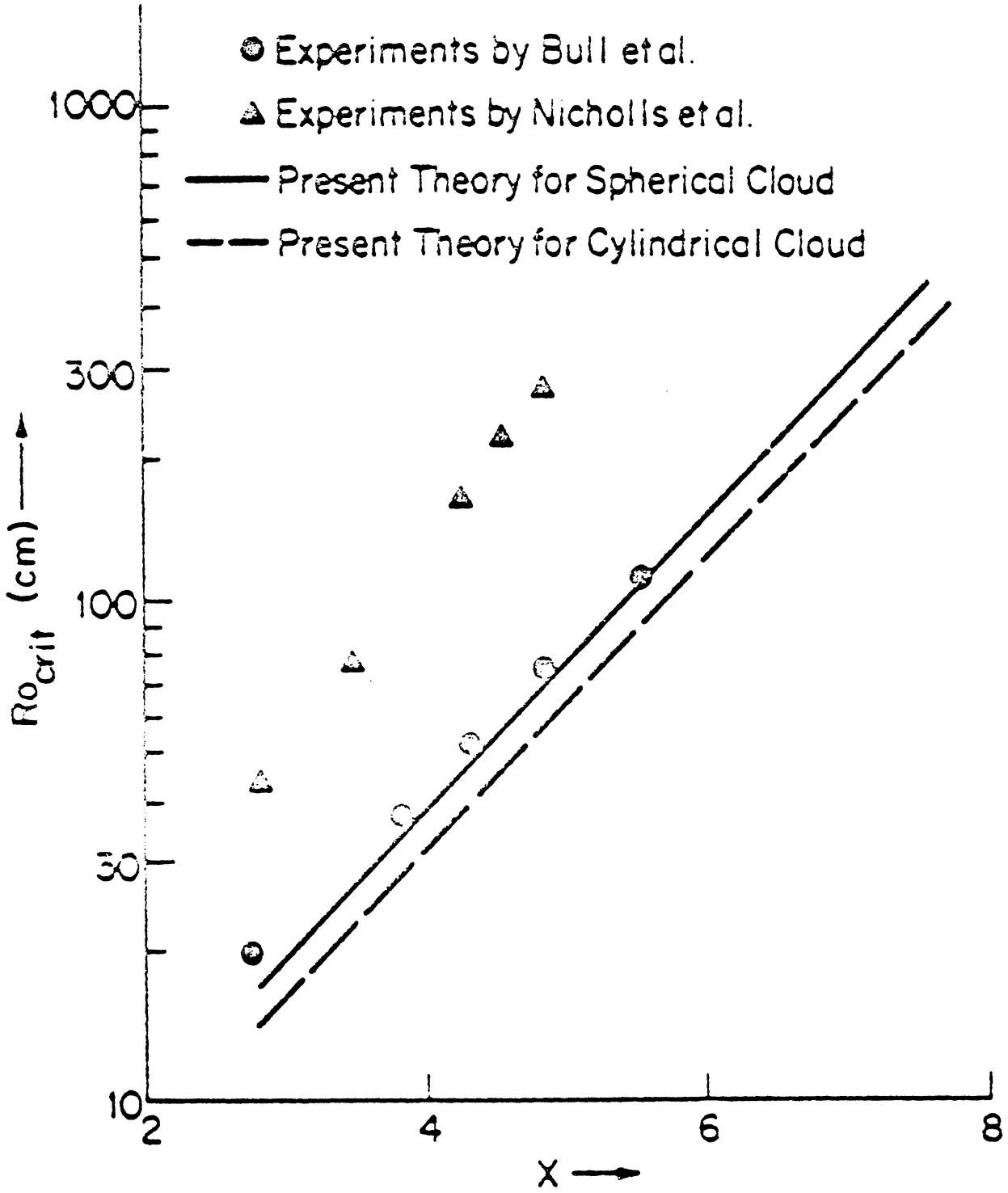

Figure 6. Theoretical and Experimental Variation of the Critical Explosion Length

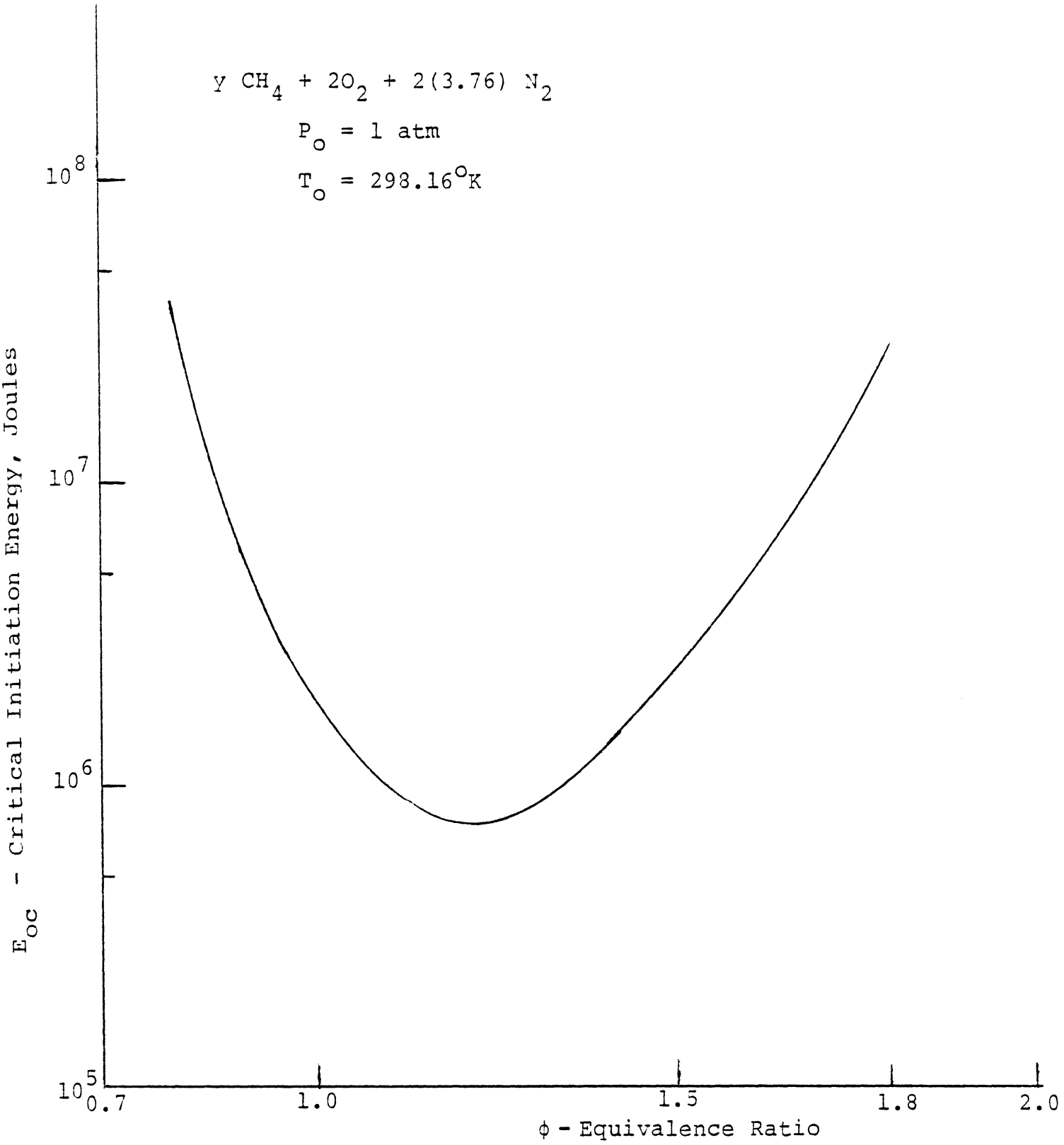

Figure 7. Theoretical Prediction of Critical Energy Versus Equivalence Ratio